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Seed Oil Based Polyurethanes: An Insight

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1. Introduction

Seed oils [SO] are cost-effective, eco-friendly and biodegradable in nature. They bear functional groups such as carboxyls, esters, double bonds, active methylenes, hydroxyls, oxirane rings and others, amenable to several derivatization reactions. Their abundant availability, non-toxicity and rich chemistry has established SO as focal point of polymer production, e.g., production of polyesters, alkyds, epoxies, polyols, polyethers, polyesteramides, polyurethanes and others. The escalating prices of petro-based chemicals, environmental and health concerns have further beckoned the enhanced utilization of SO as polymer precursors. SO have attracted enormous attention as potential source of platform chemicals, at both laboratory and industrial scale. Today, oil-seed bearing crop plants are being raised and modified for uses in areas covering biodiesel, lubricants, folk medicines, cosmetics, plastics, coatings and paints.

SO based polyurethanes [PU] occupy an important position due to their simple preparation methods, outstanding properties and versatile applications in foams, coatings, adhesives, sealants, elastomers and others [1-4]. In general, PU are prepared by chemical reaction of a diol, polyol or any oligomer or polymer containing hydroxyl groups, with an aliphatic, cycloaliphatic or aromatic isocyanate. SO serve as green precursors to diols, polyols and other -OH containing polymers offering greener raw materials in PU synthesis, replacing their petro-based counterparts. The choice of SO polyol or isocyanate is governed by the end-use application of SO PU ranging from soft and flexible to rigid PU foams, thermoplastic to thermosetting PU, flexible films to tough, scratch-resistant, impact resistant coatings and paints. It is well known that the structure of a triglyceride is very complex. Every SO has a characteristic fatty acid profile. Amongst the same species, the composition of triglycerides in a particular SO varies by weather conditions of crops and soil. Triglycerides vary by their fatty acid chain lengths, presence as well as the position of double bonds and degree of unsaturation of the constituent fatty acids. The structures of

natural SO and their derivatives, i.e., epoxies, diols, polyols, polyesters and alkyds are complex. Thus, the properties of PU obtained from SO derivatives depend on a number of factors such as (i) the type, composition and distribution of fatty acid residues in the constituent triglycerides, (ii) the number, distribution, site of hydroxyls (in the middle or closer to the end of the triglyceride chain) and level of unsaturation in the fatty triester chains of the parent diol or polyol, (iii) the type, position and structure of isocyanates used and (iv) the urethane content of the final PU [5-8].

The ingredients for the preparation of SO based PU generally comprise of a diol or polyol (containing active hydrogens) derived from SO and an isocyanate, aliphatic and aromatic such as 1,6-hexamethylene diisocyanate [HMDI], isophorone diisocyanate [IPDI], cyclohexyl diisocyanate [CHDI], L-Lysine Diisocyanate [LDI], toluylene 2,4-diisocyanate or toluylene 2,6-diisocyanate [TDI], 4,4'-methylenediphenyl diisocyanate [MDI], naphthylene 1,5-diisocyanate [ND]. PU are prepared by polyaddition reaction between the two components, often in presence of a chain extender, cross-linker or a catalyst. Today, several environment friendly routes for the production of PU have cropped up. Research has been focussed on the preparation of PU from non-isocyanate routes, and also on the use of fatty acid based isocyanates for PU production, considering the persisting challenges of polymer industry and immediate attention sought towards environmentally benign chemicals and chemical routes for the same [9-18].

SO based PU are generally flexible in nature. Generally, these PU show low T_g due to the presence of long aliphatic chains and also poor mechanical properties (owing to the presence of dangling chains). The thermal stability of SO based PU is also lower since the decomposition of urethane bonds starts at 150-200°C. Javni et al have studied the decomposition of PU from Olive, Peanut, Canola, Corn, Soybean, Sunflower, Safflower and Castor oils [7]. The decomposition involves the dissociation of urethane bonds to isocyanate, alcohol, amine, olefin and carbon dioxide. The properties of PU depend upon their crosslinking density as well as chemical composition. In an excellent review, Petrovic has highlighted the different properties of PU prepared from polyols obtained by different methods. As the properties of polyols depend upon the methods of preparation, so also the properties of PU derived therefrom. He has presented a brief outline of the effect of polyols prepared by epoxidation, hydroformylation, ozonolysis, effect of crosslinking density, and type of isocyanate on the properties of PU. He described the effect of the structure of polyols prepared by epoxidation followed by ring opening with methanol, HCl, HBr, and by hydrogenation of epoxidized Soybean oil, and showed that PU obtained from these polyols showed relatively higher glass transition temperatures and improved mechanical properties. Halogenated polyols obtained via ring opening by HCl and HBr gave PU that were less stable than ones without halogens, and had higher T_g (70°C –80°C) than the latter. Polyols obtained via hydroformylation crystallize below room temperature while those derived through hydrogenation reveal crystallization at temperature higher than room temperature. PU from non-halogenated polyols had higher thermal stability than brominated (100°C) or chlorinated polyols (160°C). Polyols with primary hydroxyls give

more stable PU than their counterparts with secondary hydroxyls. PU with high crosslink density show higher thermal stability. Hydrolytic stability of PU also depends on the degree of crosslinking, temperature, and physical state of PU. In SO based PU, although SO have ester groups susceptible to hydrolysis, long hydrophobic fatty acid chains cause shielding effect. Under highly humid conditions, urethane bonds undergo hydrolysis producing amine and carbon dioxide [1, 19].

SO are rich in various functional groups such as double bonds, active methylenes, esters, hydroxyls and others. These undergo several chemical transformations yielding numerous derivatives with versatile applications as inks, plasticizers, lubricants, adhesives, coatings and paints. Amongst various SO derivatives, those containing hydroxyl groups are used in the production of PU. These include SO based diols, triols, polyols, polyesters, alkyd, polyesteramide, polyetheramide and others (Figure 1).

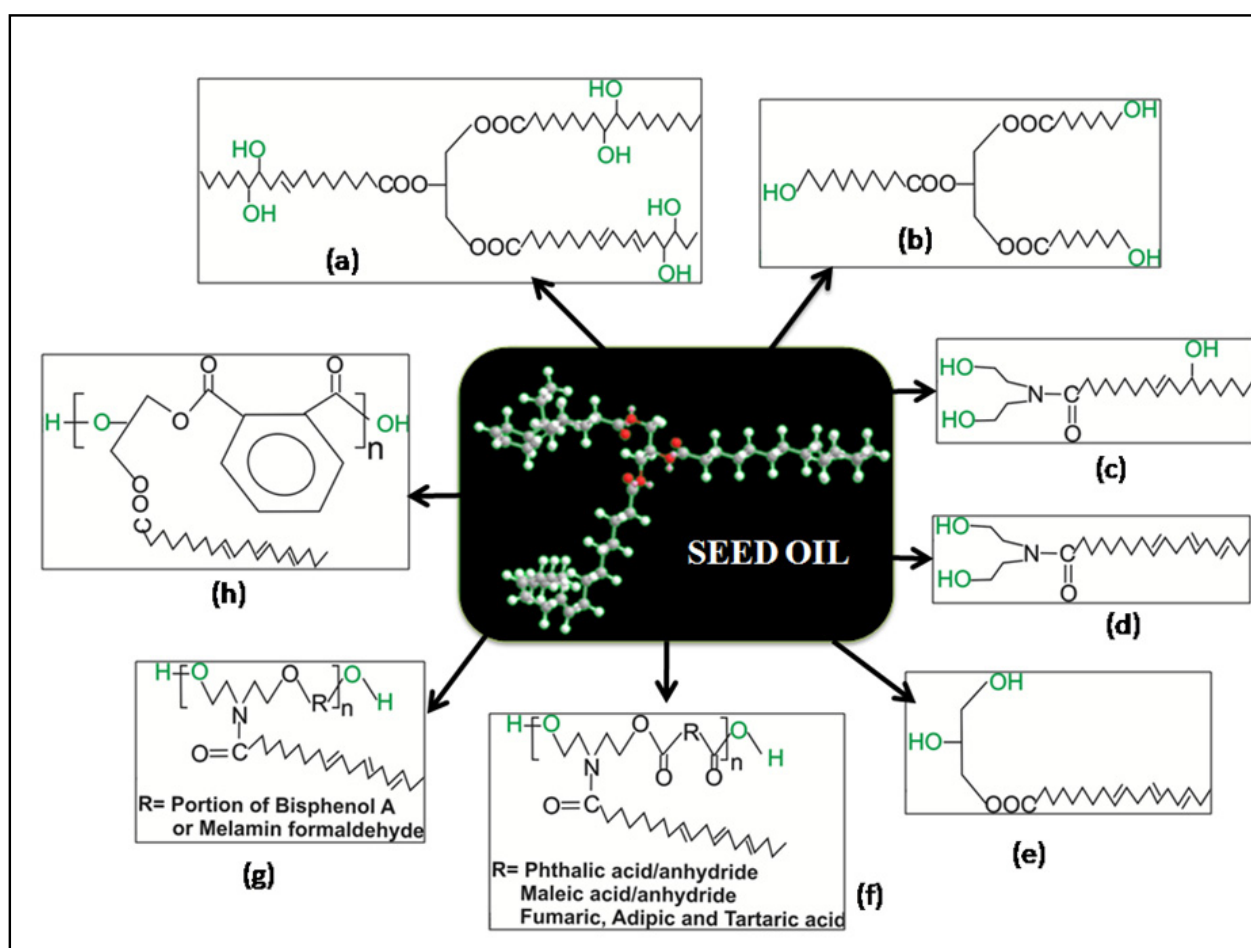


Figure 1. SO derivatives used in the production of PU (a) polyol, (b) triol, (c) fatty amide triol, (d) fatty amide diol, (e) monoglyceride, (f) polyesteramide, (g) polyetheramide, and (h) alkyd.

The chemistry of SO based PU is very vast, governed by several factors such as the type of diol or polyol, type of isocyanate, preparation method of diols or polyols, type of chain

extender, cross-linker, reaction temperature and other reaction conditions. In this chapter we have focussed on the preparation, structure and properties of PU obtained from diols, triols and polyols derived by amidation of SO termed as "SO alkanolamides". In the proceeding sections, we have also discussed the modifications of the said SO alkanolamides based PU at the forefront of PU chemistry such as SO based metal containing PU, PU hybrids, composites for applications mainly in coatings, paints and foams.

2. SO based diols

The most excessively used SO based diol in PU production is fatty amide diol or fatty alkan-diol-amide [FAD] (Figure 2). FAD is obtained by the base catalysed amidation of SO with diethanolamine. The structure of FAD is determined by the fatty acid composition of the starting SO.

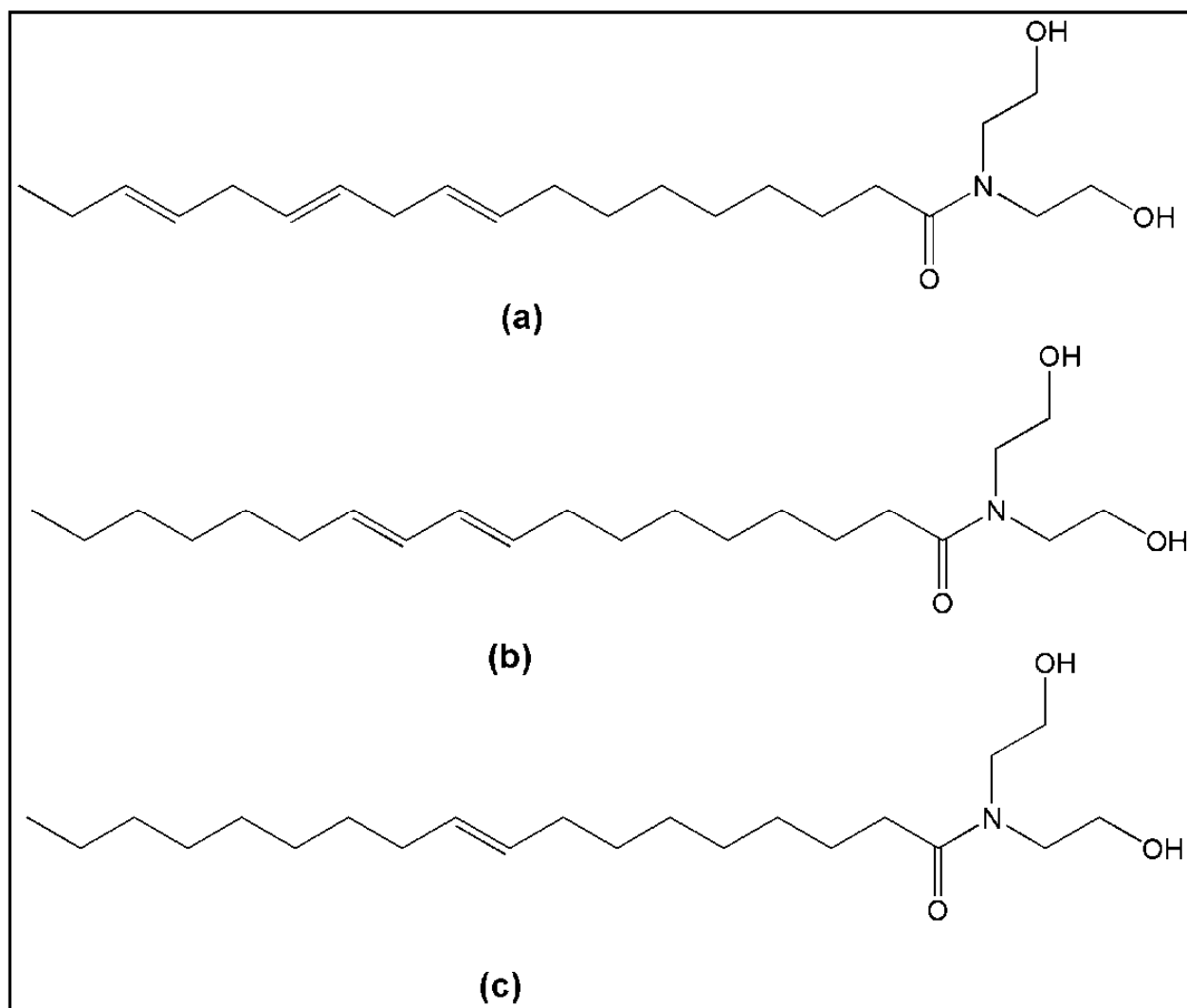


Figure 2. Figure 2. FAD from (a) Linseed (35.0-60.0 % Linolenic acid), (b) Soybean (43.0-56.0 % Linoleic acid) and (c) Karanj (44.5–71.3 % oleic acid), Nahor (55-66% oleic acid) , Jatropha (37-63 % oleic), Olive (65-80 % oleic acid)

The reaction proceeds by nucleophilic acyl substitution bimolecular (SN₂) reaction mechanism. As the name suggests, FAD contains an amide group, with two hydroxyl ethyl groups directly attached to amide nitrogen along with the pendant aliphatic chain of SO. FAD is derived from different SO such as Linseed (*Linum ussitassimum*), Soybean (*Glycine max*), Karanj (*Pongamia glabra*), Nahor (*Mesua ferrea*), Jatropha (*Jatropha Curcus*), Olive (*Olea europea*), Coconut (*Cocos nucifera*) and others [20-30] (Figure 2). FAD is used as raw material for various polymers such as PU, poly (esteramide) and poly (ether amide).

3. PU from SO FAD

FAD can be treated with an isocyanate such as TDI, IPDI, HMDI, MDI, ND, CHDI and LDI forming poly (urethane fatty amide) (Figure 3) [FADU] [31].

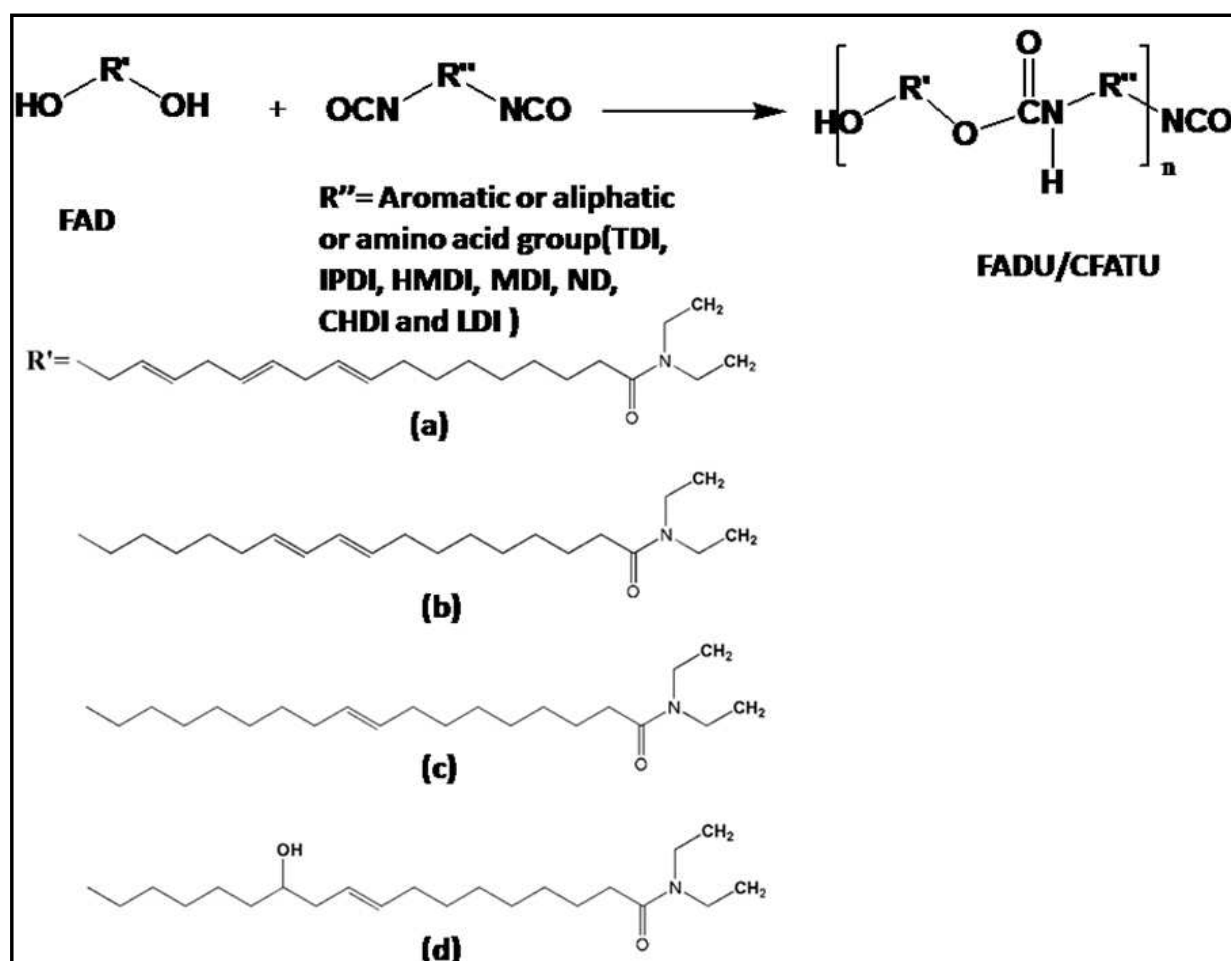


Figure 3. FADU from (a) Linseed, (b) Soybean (c) Karanj, Nahor, Jatropha, Olive and (d) Castor

For the first time, Linseed oil [LO] derived FAD [LFAD] was treated with TDI by one-shot technique to prepare PU [LFADU] as introduced by Ahmad et al [32] (Figure 4).

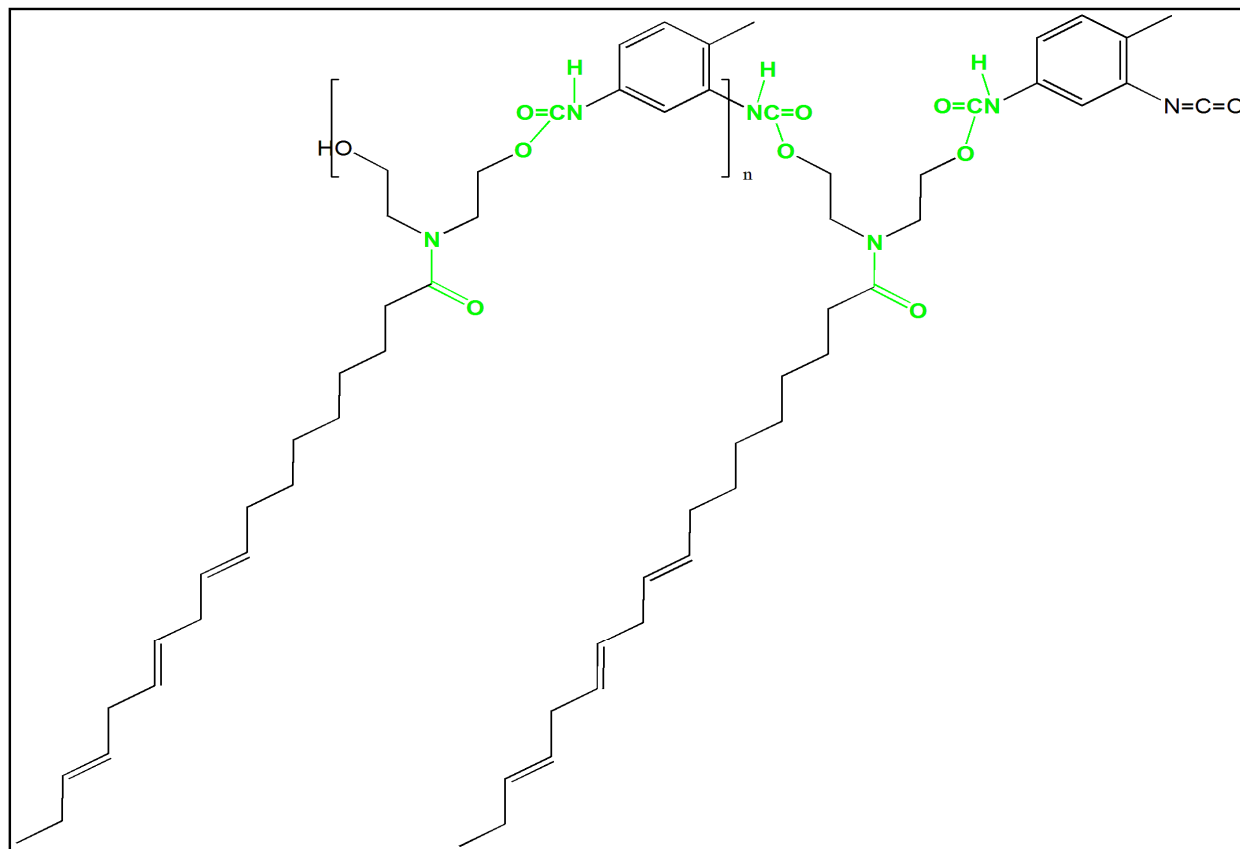


Figure 4. Chemical structure of LFADU.

The structure of LFADU was established by spectral analyses. FTIR, ^1H NMR and ^{13}C NMR spectra showed the presence of the main characteristic absorption bands of parent SO [32]. Along with these bands, additional absorption bands are observed supporting the presence of urethane groups in the backbone of LFADU such as those at 3375cm^{-1} for hydroxyl groups, 1716.11 cm^{-1} for urethane carbonyl (str), 1227.56cm^{-1} for C–N of urethane groups, 1735cm^{-1} typical for carbonyl (str) of TDI. The characteristic peaks for hydrogen bonded and non-hydrogen bonded protons of $-\text{HNCOO}-$ appear at $7.99\text{--}7.82\text{ppm}$ and $7.1\text{--}6.9\text{ppm}$, respectively. The aromatic ring protons of TDI occur at $7.5\text{--}7.22\text{ ppm}$. The peaks of $-\text{HNCOOCH}_2-$ are observed at $4.1\text{--}3.9\text{ppm}$ and for CH_3 of TDI appear at 2.25ppm . ^{13}C NMR spectrum also shows the presence of characteristic peaks of LFADU at 17ppm (CH_3 of TDI), 143.97ppm $\{-\text{NH}-(\text{C O})-\text{O}-\}$ and 137.46 , 136.2 , 134.4 , 125.94 , 125.4 , 116.0 ppm (aromatic ring carbons of TDI). TGA thermogram of LFADU has shown four step degradation pattern, at $260\text{ }^\circ\text{C}$ (27% weight loss), $360\text{ }^\circ\text{C}$ (21% weight loss), $505\text{ }^\circ\text{C}$ (40% weight loss), $640\text{ }^\circ\text{C}$ (9% weight loss) corresponding to the degradation of urethane, ester, amide and hydrocarbon chains, respectively.

PU from Karanj or *Pongamia glabra* [PGO] oil [PFADU] has also been prepared by similar method. PU obtained from both FAD showed similar structure except for the difference in the structure of pendant fatty amide chains attributed to the variation in the structure of the parent SO chain [33] (Figure 5).

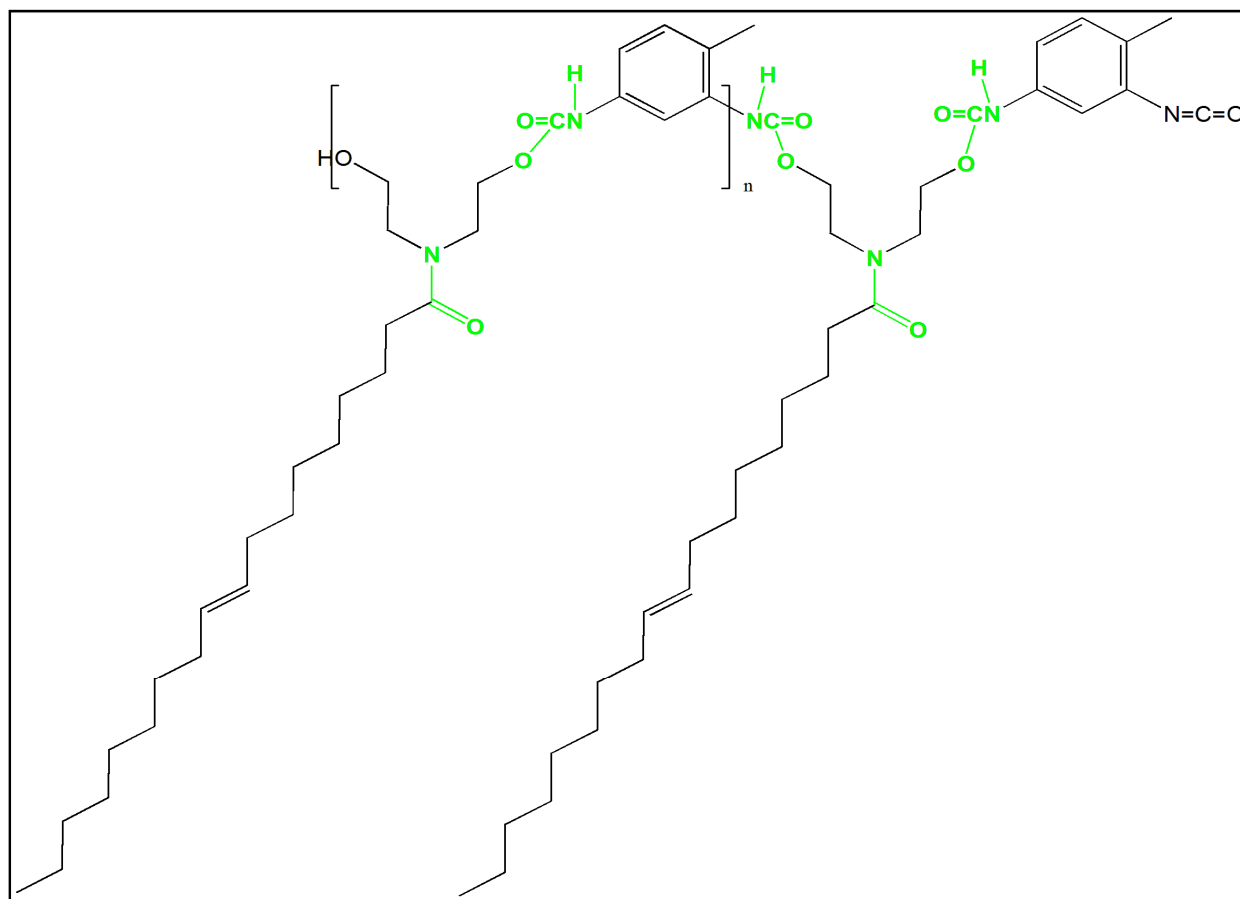


Figure 5. Chemical structure of PFADU or NFADU

The thermal degradation of PFADU was observed at 177°C and 357°C, with 5% weight loss occurring at 200°C attributed to the entrapped solvent and moisture, 10wt% loss at 225 °C, attributed to the decomposition of urethane moieties, 50wt% and 80wt% losses at 390 °C and 455 °C, respectively, attributed to the degradation of the aromatic ring and aliphatic pendant fatty alkyl chains, respectively.

It was observed that in both LFADU and PFADU, beyond 1.5moles loading of TDI, formation of some lumpy aggregates occurred. Upto 1.5 moles of TDI addition, it is speculated that the isocyanate groups of TDI react with hydroxyl groups of FAD forming PU linkages. Beyond this amount, any additional isocyanate added reacts with the urethane groups of LFADU or PFADU forming allophanate groups (secondary reaction). The final PU attains very high viscosity and crosslinking, so much so that the formation of lumpy aggregates occurs and PU is deprived off its free flowing tendency.

Karak and Dutta have reported the production of PU by amidation and urethanation of methyl ester of *M. Ferrea* or Nahor oil [NO], rich mainly in triglycerides of linoleic, oleic, palmitic and stearic acids. They investigated the structure and physico-chemical aspects of FADU from NO [NFADU] [26].

3.1. PU as coatings

LFADU has free $-OH$, $-NCO$, aliphatic hydrocarbon chains (from parent LO), amide and urethane groups, which make it an excellent candidate for application in protective coatings (Figure 4). LFADU coatings undergo curing at ambient temperature ($28-30^{\circ}C$) by three stage curing phenomenon, (i) solvent evaporation (physical process), (ii) reaction of free $-NCO$ groups of LFADU with atmospheric moisture, and (iii) auto-oxidation. These coatings show good scratch hardness (2.5kg), impact resistance (200lb/inch), bending ability (1/8inch) and chemical resistance to acid and alkali. PU from PGO [PFADU] has shown moderate antibacterial behavior against *Salmonella* sp. with good scratch hardness (1.9kg), impact resistance (150lb/inch), bending ability (1/8inch), and gloss (46 at 45°) [33]. LFADU coatings have shown superior coating properties than PFADU owing to the fatty acid composition of parent oils (PGO, a non-drying oil has higher content of oleic acid while LO, a drying oil, is rich in linolenic acid).

Karak and Dutta have reported the use of NFADU coatings with very good alkali resistance (Figure 5)[32].

3.2. PU as hybrids

Organic-inorganic hybrid materials have been developed with FADU as organic constituent and metal/metalloid as inorganic component to improve the performance and broaden the applications of PU (Figure 6).

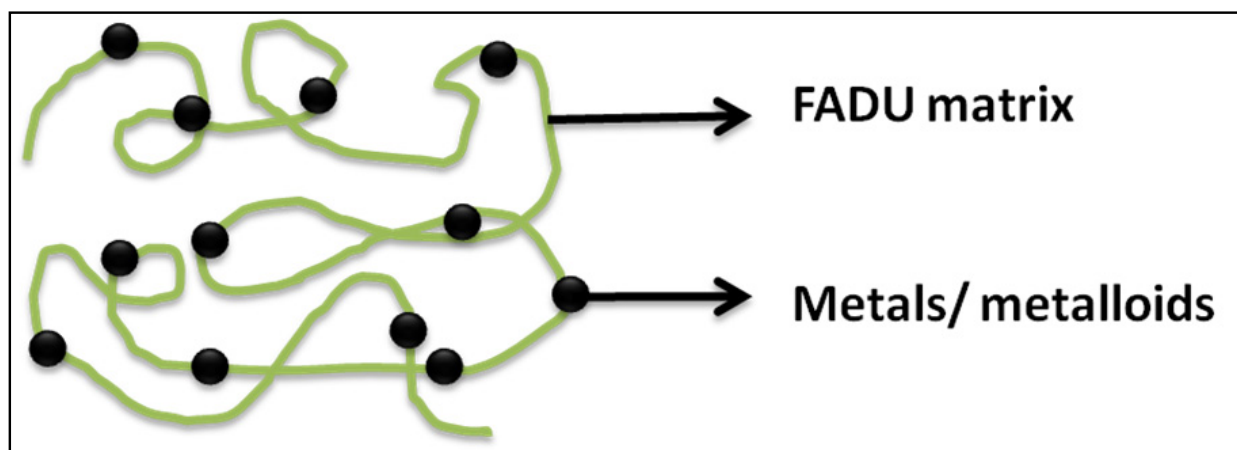


Figure 6. PU as hybrids

In one report, Zafar et al. have prepared organic-inorganic hybrids by using boric acid as inorganic content and PFADU as organic matrix [B-PFADU] [34]. B-PFADU was characterized by standard spectral techniques and physico-chemical methods. B-PFADU performed well as protective coatings in terms of physico-mechanical and chemical resistance tests. B-PFADU showed no change in water and xylene upto 15 days. However, slight deterioration in performance was observed in alkali and acid media, correlated to the presence of $-O-B-O-$ which is susceptible to hydrolysis on exposure to these media. B-

PFADU showed high activity against *E. coli* (Zone of inhibition: 21-30 mm) and moderate activity against *S. aureus* (Zone of inhibition: 16-20 mm). The reason can be the presence of urethane, amide, and hydroxyl groups in the polymer backbone, which can presumably interact with the surface of microbes, causing antibacterial action. B-PFADU can be used as an antibacterial agent as well as coating material.

In another work, Ahmad and co-workers developed LFADU hybrid material with tetraethoxy orthosilane [TEOS] as inorganic constituent in the hybrid material [Si LFADU] by in situ silylation of LFAD with TEOS (at 80 °C) followed by urethanation with TDI (at room temperature) [35]. Along with the typical absorption bands for LFADU, additional absorption bands were observed at 484 cm^{-1} (Si–O–Si bending), 795 cm^{-1} (Si–O–Si sym str) and 1088 cm^{-1} (Si–O–Si assym str) in FTIR due to the presence of -Si–O–Si- bond in the hybrid backbone. Hydroxyl value decreases while refractive index and specific gravity increase with the loading of TEOS in Si LFADU, supporting the formation of the hybrid materials by insitu silylation and urethanation reaction. Optical micrograph of Si LFADU showed the presence of SiO_2 particles surrounded by LFADU (Figure 7).

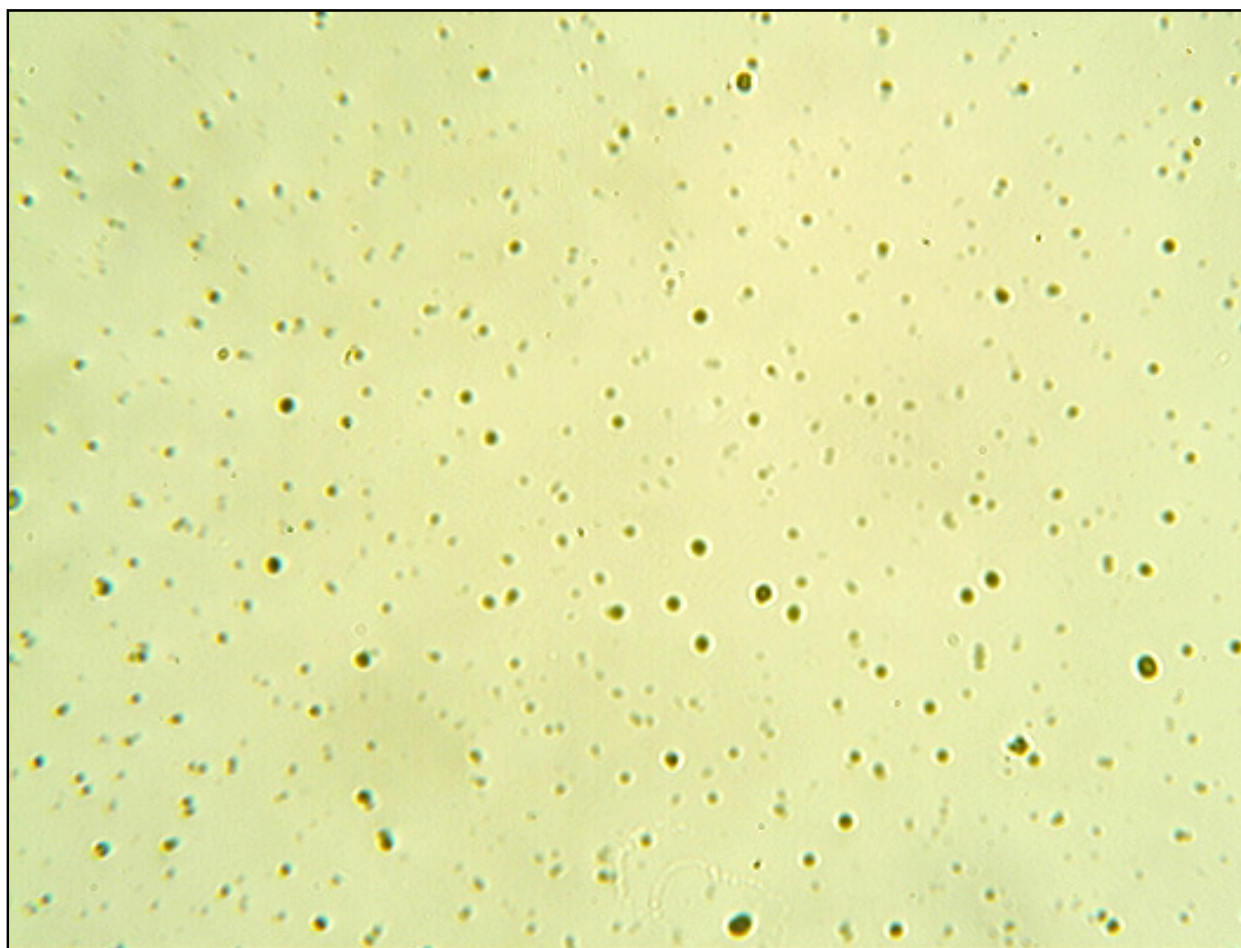


Figure 7. Optical micrograph of Si LFADU

Si LFADU formed hybrid coatings by simple curing route at ambient temperature, over mild steel panels of standard sizes with improved gloss and scratch hardness. SiO_2 domains

also improved adhesion with the penal surface exhibiting good scratch hardness, bending ability (1/8 inch) and impact tests (150 lb/inch) correlated to the synergism showed by both the components, LFADU backbone imparting flexibility and gloss, while the inorganic domains conferring excellent adhesion and hardness [36].

The corrosion rate (CR) of Si LFADU is much lower (3.08×10^{-4} mm per year) relative to LFADU (3.124 mm/year) In 3.5wt% HCl, with inhibition efficiency (IE%) 99.77. In 3.5% NaOH, CR and IE% were found as 1.26×10^{-3} mm per year and 99.34, respectively. Si LFADU formed uniform and well adhered coating over the metal substrate which prohibits the permeation of corrosive media. The protection mechanism is purely through barrier action attributed to the hydrophobic inorganic content [37, 38]. Coating remained intact when subjected to corrosive media for 192 h as supported by the constant value of polarization resistance ($R_p = 1.22 \times 10^4$ Ohm in NaOH and 7.7×10^5 Ohm for HCl). Thermal studies showed four step degradation, thermal stability increasing with higher inorganic content, with two glass transition temperatures (T_g) as observed at 115 °C and 155 °C in DSC thermogram with safe usage upto 200 °C.

3.3. PU as composites

Composite materials from FADU have not been prepared yet. In their recent research, Zafar et al have developed composites from FADU using metal oxides and organo-montmorillonite clay [OMMT] (Cloisite 30B; modified by an alkyl ammonium cation bearing two primary hydroxyl functions, alkyl group is tallow containing $\approx 65\%$ C18, $\approx 30\%$ C16, and $\approx 5\%$ C14, Southern Clay product) as modifiers added in very lower amounts to FADU matrix (unpublished work). The sole aim behind the development of these composites was the improvement in performance of FADU materials in terms of thermal stability, physico-mechanical and corrosion or chemical resistance performance, and also antimicrobial behavior relative to the pristine material for high performance applications. MMT occurred as nano-sized aggregates with size ranging from 37 to 100 nm as observed by Transmission Electron Micrography [TEM]. The thermal stability of FADU/ MMT was found to increase with increased MMT loading. These composites may be used as protective coatings in future. Zafar et al have also developed FADU/MnO composites, with good antifungal behavior. MnO occurred as needles self-assembled in “lemon slices” morphology as observed in optical micrograph (Figure 8). The said composite material may find application as antimicrobial agent in coatings and paints.

PU composites were prepared by the dispersion of conducting polymer poly (1-naphthylamine) [PNA] in LFADU matrix in amount ranging from 0.5–2.5 wt% by conventional solution method as reported by Riaz et al [39]. At lower levels, the composites were very fragile in nature. The polymerization of PNA occurred through N–C(5) linkages of 1-naphthylamine units as confirmed by FTIR spectra. PNA also reacted with free isocyanate groups of TDI forming urea linkages, as also supported by spectral analysis. UV visible spectra also confirmed the formation of urea linkages between LFADU and PNA. TEM micrographs showed the average particle size as 17–27 nm. Nanoparticles appeared as

smaller aggregates which later on formed larger aggregates. XRD analysis revealed purely amorphous nature of composites. With the increase in the loading of PNA in the composites, the distortion and torsional strain increased in the composites due to higher urea linkages. It was found that as the percent loading of PNA in the composites increased, their electrical conductivity values also increased; however, these values fell in the semi-conducting range, which was much higher relative to the conductivity values obtained with very high loading of PNA in previously reported composites. The improved electrical conductivity values of LFADU/PNA composites can be correlated to the hydrogen bonding and urea type linkages formed between the two polymers, which provide the path to charge conduction [40,41].

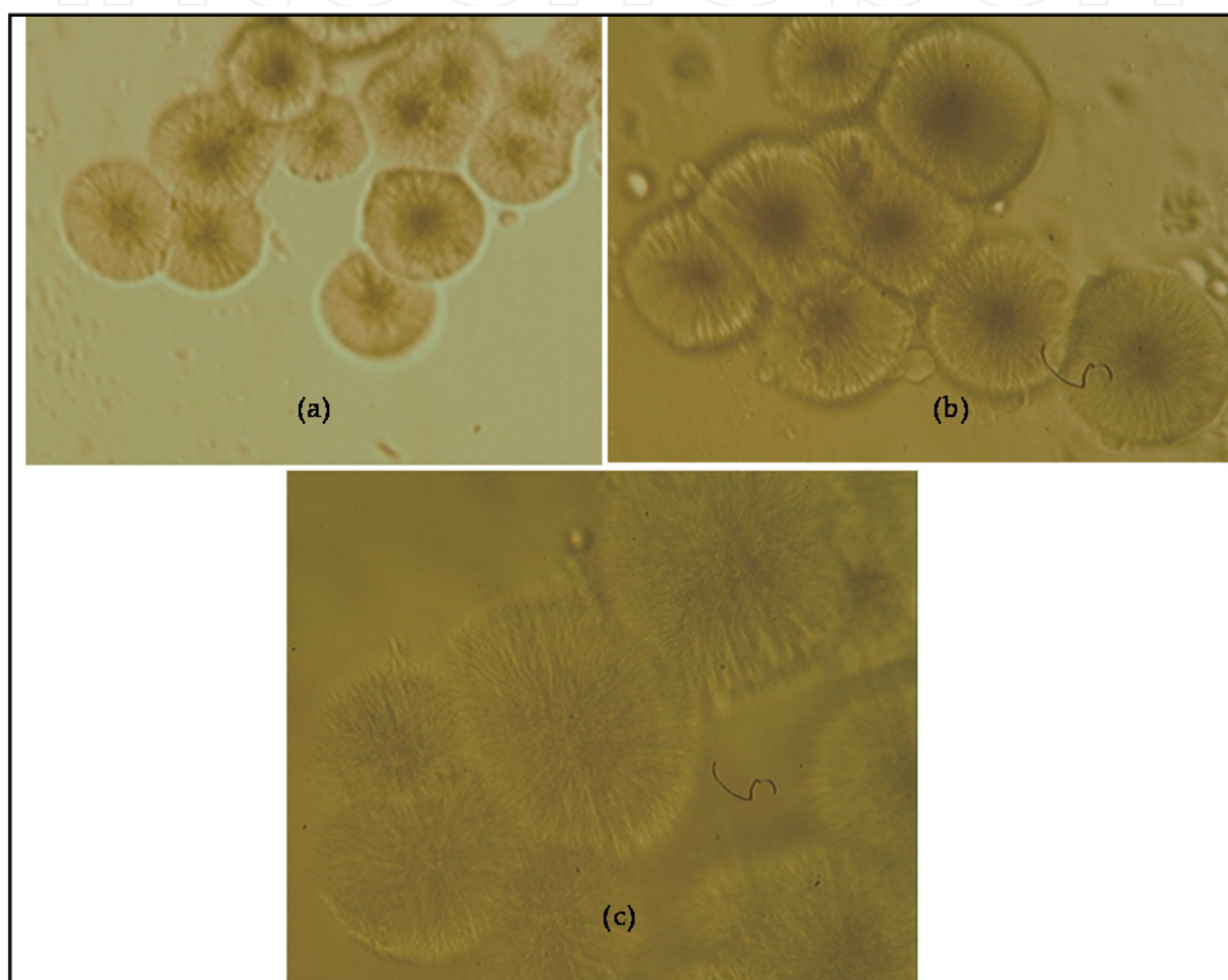


Figure 8. Optical micrographs of FADU/MnO (a) 100 X, (b) 200 X, (c) 500 X

4. SO based triol

Castor oil (CO) is obtained from seeds of *Ricinus communis* or Castor belonging to the family *Euphorbiaceae*. It is non edible oil. The crop is cultivated around the world because of the commercial importance of its oil. India is the world leader in castor production and dominates the international CO trade. Worldwide castor production was about 1.4 million metric tons during the year 2009 with an average yield of about 956 kg ha⁻¹. Ricinoleic acid

(12-hydroxy-9-octadecenoic acid), hydroxyl containing fatty acid, is the major component of CO, and constitutes about 89% of the total fatty acid composition. Castor seed products have widespread applications in many industries like paints, lubricants, pharmaceuticals and textiles. Today, the importance of these products has grown manifold because of their biodegradable and eco-friendly nature.

Due to the inherent hydroxyl functionality, CO stands as an excellent natural raw material for the development of PU. CO derived PU are flexible due to long aliphatic triglyceride dangling chains [42]. CO has three hydroxyl moieties in one triglyceride molecule. On amidation, CO yields fatty amide triol or alkan-triol-amide [FAT], which bears two hydroxyl ethyl groups directly attached to amide nitrogen, as well as one hydroxyl group in the pendant fatty chain obtained from the parent CO. Thus, CO derived FAT [CFAT] acts as SO derived triol (Figure 9). Rao et al prepared acrylated CFAT as a multifunctional amide for photocuring [31, 43, 44].

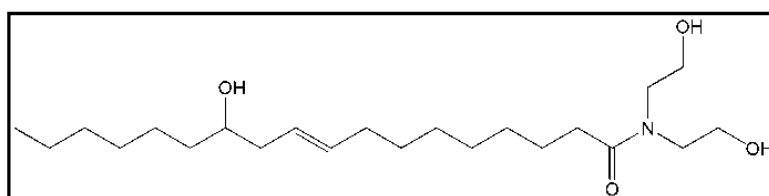


Figure 9. CO (87-90 % Ricinoleic acid) derived FAT [CFAT]

5. PU from SO FAT

CFAT on chemical reaction with TDI by one shot technique yields CFATU (Figure 10), with an additional crosslinking site (hydroxyl group) conferred by parent CO containing 89% ricinoleic acid. Contrary to LFADU and PFADU, where the permissible limit of TDI addition is 1.5 moles, in CFATU, at 1.2 moles of TDI addition, CFATU becomes highly viscous. The difference prevails due to the additional hydroxyl functionality in CFATU, which presumably makes possible higher inter and intra crosslinking sites relative to LFADU and PFADU. As also observed in LFADU and PFADU, the physico-chemical characteristics such as specific gravity, inherent viscosity and refractive index increase, while hydroxyl and iodine values decrease on increasing the content of TDI in PU. The thermal degradation occurred in the temperature range of 150–390 °C. The decomposition observed at earlier temperature range may be attributed to the thermal degradation of urethane linkages followed by the volatilization of the decomposition products while that at higher temperatures is correlated to the degradation of amide bond, aromatic ring and aliphatic alkyl chain of the fatty acid, respectively, followed by the volatilization of the decomposition products [45, 46].

5.1. PU as coatings

CFATU coatings have been prepared and their physico-mechanical, thermal as well as corrosion resistance behavior has also been investigated [31]. CFATU have been further modified for improvement in their performance as discussed in proceeding sections.

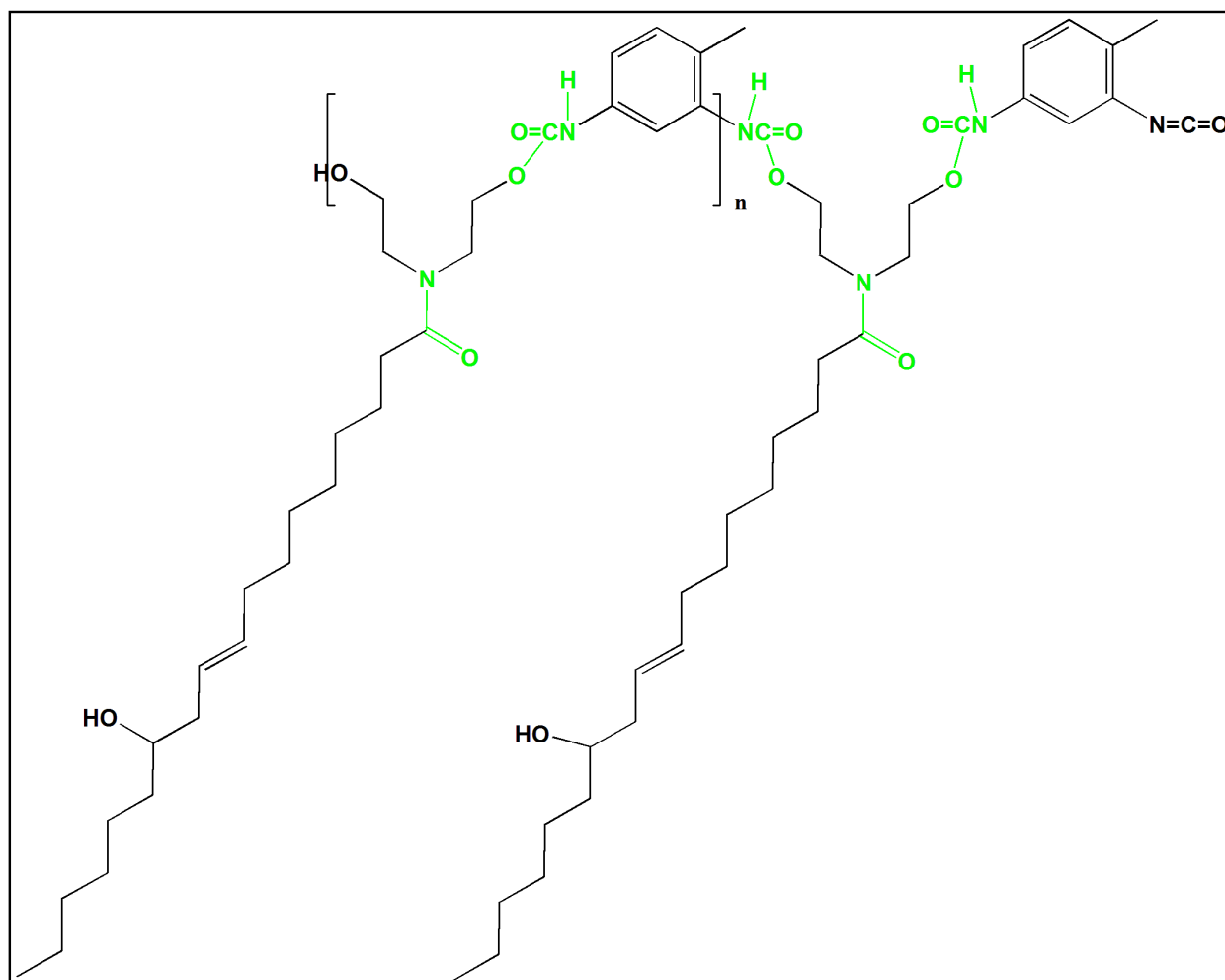


Figure 10. Chemical structure of CFATU

5.2. PU as hybrids

Ahmad et al have reported the preparation and characterization of metal containing CFATU [47]. They treated CFAT with zinc acetate (5, 10 and 15 wt%) and TDI (25–75 wt%) to prepare metal containing CFATU [MCFADU] “in situ” by microwave [MW] assisted preparation method in a domestic MW oven. During the preparation, it was observed that MCFATU with > 5wt% zinc acetate formed gel. While the conventional preparation method of LFADU, CFATU, PFADU and NFADU requires 8-12 hours, CFATU is obtained in 4 minutes by MW assisted preparation method. By molecular interactions with the electromagnetic field and heat generated by molecular collision and friction, the reaction is facilitated to occur in much reduced time periods under the influence of MW irradiations. In this reaction, hydroxyl groups of CFAT react with zinc acetate and TDI successively. Curing of MCFATU is a two step process occurring by solvent evaporation (physical phenomenon) followed by the second stage curing (a chemical process) where free –NCO groups of MCFATU react with the atmospheric moisture to form urethane and amino groups through addition reaction. MCFATU acted as good corrosion protective coatings for mild steel. The best physico-mechanical properties (scratch hardness 3.5 kg, impact resistance

150lb/inch, and bending ability 1/8 inch) were achieved at 5wt% loading of zinc acetate and 55 wt% of TDI, when evaluated by standard methods and techniques. The corrosion protection efficiency of the same was evaluated by potentiodynamic polarisation measurements [PDP] in aqueous solution of 3.5wt% HCl (CR 4.51×10^{-3} mm/year; IE% 96.23), 3.5wt% NaOH (CR 1.36×10^{-3} mm/year; IE% 90.81); 3.5wt%NaCl (CR 2.25×10^{-3} mm/year; IE% 94.50) and tap water (Cl⁻ ion 63 mg/L; Conductivity 0.953 mS/A) (CR 3.56×10^{-3} mm/year; IE% 98.35).

5.3. PU as composites

CFATU composites were developed by the introduction of MMT clay [48] and nano sized ZnO by Zafar et al [unpublished work]. Morphology of the composites as studied by TEM revealed the presence of nanosized globules of size ranging between 15-120 nm in CFATU/OMMT (Figure 11), and ZnO in CFATU/ZnO composites occurring as nano-sized spindles of diameter 50-60nm (Figure 12). Both the composite materials may find application as corrosion protective coatings for mild steel. CFATU/ZnO composites also act as excellent antifungal agents against common fungal strains such as *Candida albicans*, *Candida krusei*, *Candida glabrata* and *Candida tropicalis*.

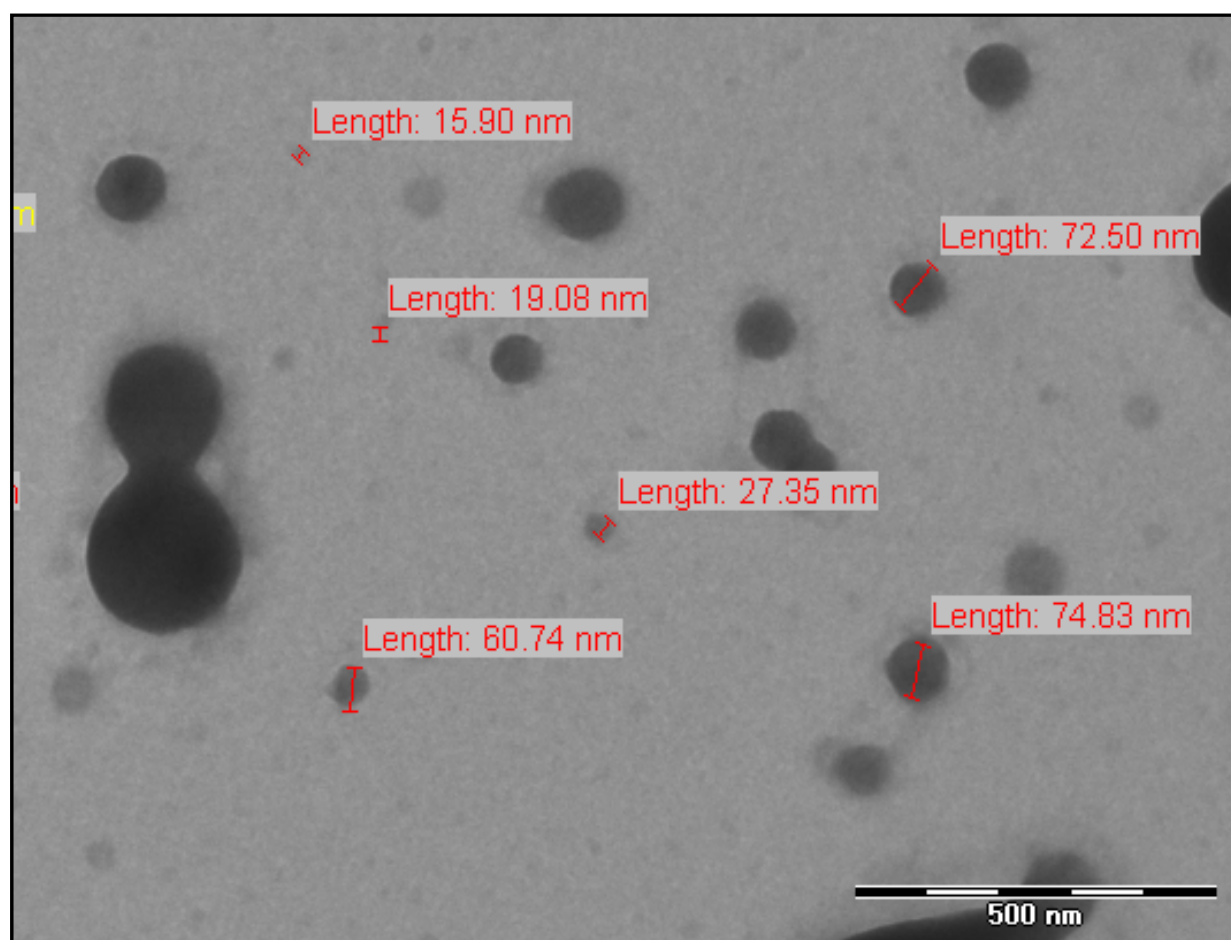


Figure 11. TEM of CFATU/OMMT

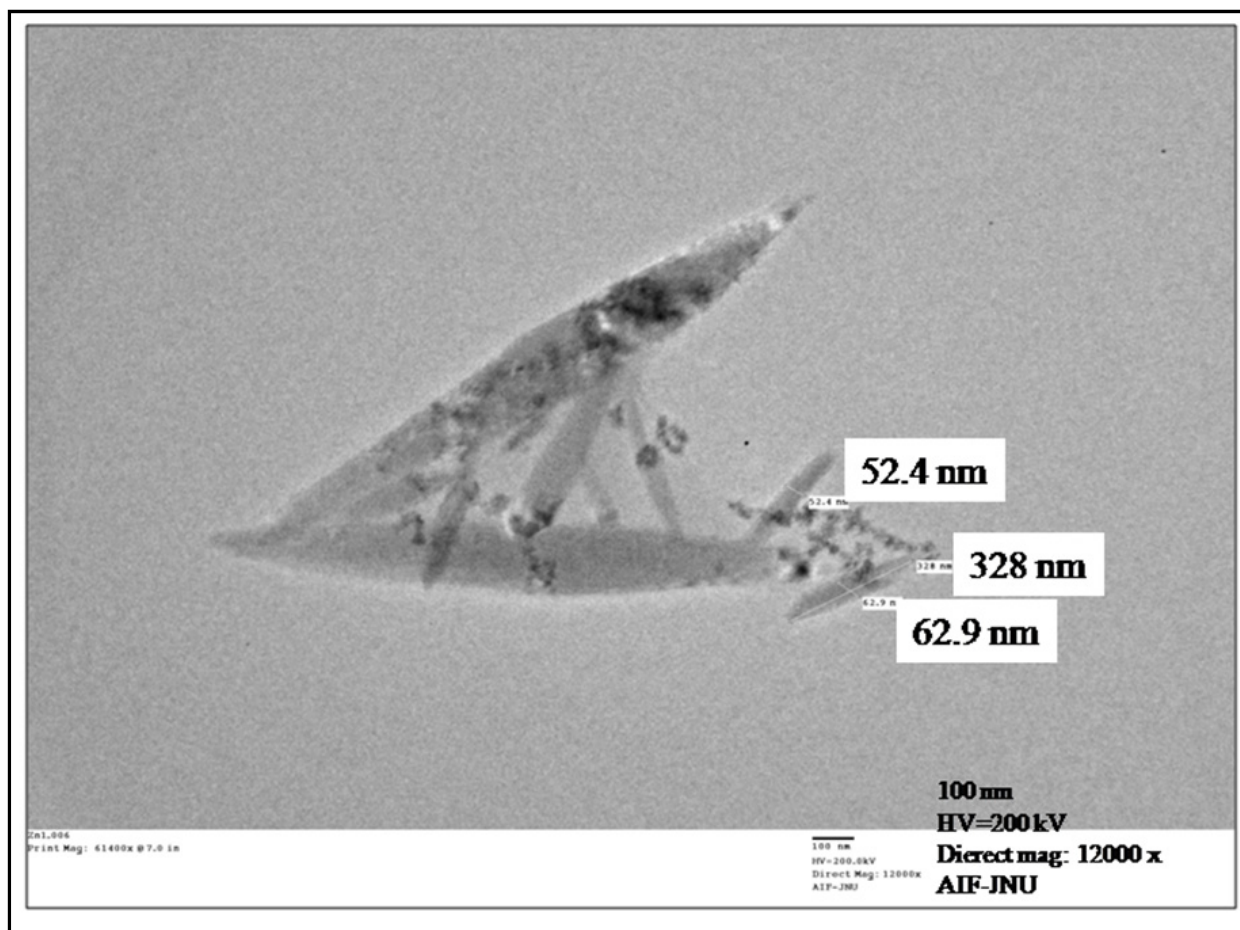


Figure 12. TEM of CFATU/ZnO composite

6. SO based polyols

SO derived polyols serve as the most important oleochemicals for PU production. Some of the SO polyols are derived through various chemical reactions such as epoxidation followed by hydration, ring opening by methanol, acids such as HBr, HCl, hydroformylation, ozonolysis of SO, others are naturally available polyols such as *Ricinus communis* or CO and Lesquerella oil. As discussed previously, the properties of PU also depend upon the type of polyol and the method by which the polyol is derived. In SO polyols, in general, hydroxyl groups are present in the middle of the triglyceride chains. Due to this, in cross linked polyols, the pendant or dangling chains provide steric hindrance to cross-linking, they do not support stress under load and act as plasticizers. In SO polyols, there is difference in the length of elastically active network chains (EANC) and elastically inactive network chains or dangling chains (DC). This variation is also passed onto their respective PU. The properties of PU thus also depend upon the content of EANC and DC, i.e., the number and position of hydroxyl groups. The number of hydroxyls on each chain in SO polyols and their stereochemistry are also variable depending upon the hydroxylating agents, hydroxylating method and other reaction conditions. For example, polyols obtained by ozonolysis and hydrogenation bear hydroxyl groups at terminal position.

SO polyols may also undergo amidation with diethanolamine to yield fatty amide polyols (FAP) [49]. Similar to FAD and FAT, FAP also house two hydroxyl ethyl amides directly attached to amide nitrogen and multiple hydroxyl groups located on the pendant fatty alkyl chains, which were part of the triglyceride molecule in parent SO bearing double bonds at the site of hydroxyl groups in FAP. The properties of SO polyols obtained by either method mentioned previously, also influence the properties of FAP. Hydroxylated, hydroxymethylated, carboxylated SO followed by their amidation yield polyols with higher number of hydroxyl groups with improved distribution [50-56]. These are ideal candidates to produce PU foams. The approach has been accomplished on CO, LO, PO, Rapeseed, Safflower, Soybean oils and refined bleached deodorized Palm Kernel Olein. These polyols have been used as non-ionic surfactants in the household and cosmetic industries and also to produce PU foams on treatment with suitable isocyanates. Such polyols prove to be advantageous over CO as they can be incorporated in higher amounts during PU formulations. Foams obtained show improvement in terms of high close cell contents, good dimensional stability and compression strength.

6.1. PU foams from SO FAP

Alkanolamide polyols serve as excellent starting materials for PU foams [50-56]. The variations in fatty acid components of starting SO, number and position of hydroxyl groups and also the presence of dangling chains in the polyol confer differences in performance and cellular structures in PU foams. The hydroxyl content of PU determines the suitability of PU foams ranging from flexible to rigid foams. A. Palaniswamy et al. produced PU foams from FAP derived from PO and Polymeric Diphenylmethane Diisocyanate (PMDI) by hand foaming. It was found that the decreased FAP content led to increase in compressive strength and density of PU foam [50]. In another research work, they have produced PU foams from PMDI and CO, in the presence of stannous octoate as catalyst and Tegostab by hand mixing process with carbon dioxide as the blowing agent generated from reaction between excess PMDI and water. PU foams with varying FAP content, catalyst and molecular weight of poly propylene glycol were studied with respect to their effect on density and compression strength [50, 51].

6.2. PU foams from SO based FAD epoxies

The epoxidized oil based alkanolamides are also classified as polyols for PU foams [56, 57]. PU show low thermal stability, thus with view to improve the thermal stability and mechanical properties of PU, heterocyclic groups such as isocyanurate, imide, phosphazene and oxazolidone, are incorporated in SO PU. The latter is formed by the chemical reaction between an oxirane ring and isocyanate in presence of a catalyst, the approach improving both thermal stability as well as stress-strain properties of the modified product with respect to the pristine material. PU foams derived from epoxidised alkanolamides show better compression strength, thermal conductivity, close cell contents

and dimensional stability relative to plain alkanolamide PU. However, in some examples, a part of epoxy content is lost during amidation reaction occurring at higher temperatures. Thus, it became imperative to determine ideal reaction conditions for amidation to retain maximum number of epoxidized rings, which was attempted by Lee et al and characterized by high performance liquid chromatography and gas chromatography [55, 56].

7. SO based polymers for PU production

As discussed earlier, SO undergo numerous transformations yielding various derivatives. Some of these derivatives bearing (inter or intra located) hydroxyls serve as excellent starting materials for PU production. A large number of PU are prepared from SO polymers such as polyesters, alkyds, polyesteramides, polyetheramides [Figure 1], which find profound applications in paints and coatings.

8. Summary

FAD, FAT and FAP serve as good starting materials for PU production. LFADU, PFADU, CFATU have similar structural characteristics; the difference being due to the pendant fatty amide chains attributed to the fatty acid composition of the parent SO. LFADU, PFADU, and CFATU are formed at a particular NCO/OH ratio. An astonishingly abnormal rise in viscosity was observed in LFADU and PFADU above 1.5 moles and in CFATU above 1.2 moles of addition of TDI, followed by the formation of lumpy aggregates. According to the general chemistry of PU, a particular NCO/OH ratio is required for a particular application. The best properties in PU are achieved when this ratio is kept as or closer to 1 or 1.1, i.e., when one equivalent weight of isocyanate reacts with one equivalent weight of polyol, to achieve the highest molecular weight. In certain applications this ratio is kept well below the stoichiometry (higher hydroxyl content relative to isocyanate) to obtain low molecular weight PU for applications as adhesives and coatings as described in the chapter. NCO/OH ratio is varied by the formulator based on the type of end use application of PU. Properties of PU mentioned here also depend on the chemical route of raw materials (polyol, isocyanate), functionality and type of the raw materials (diol, triol, polyol and isocyanates-aliphatic, aromatic), the number of urethane groups per unit volume, non-isocyanate PU, as well as other structural differences such as the presence of modifiers (acrylics, metals, nanosized metal oxides, MMT clay).

The preparation through MW technique offers advantages of reduced times and improved yield. Most of these PU are used for coatings and foams. The incorporation of inorganic constituent led to improved thermal and hydrolytic stability as well as coating performance of PU. Another area that is presently being explored is the preparation of green PU from fatty isocyanates or non-isocyanate PU. Due to their numerous applications and advantages SO PU have been extensively studied and extensive research is still going on.

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